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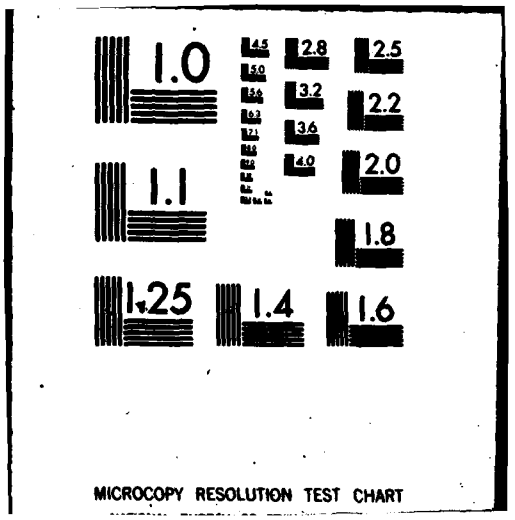
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Research on the inelastic scattering of light by elementary excitations in solids has provided information about the nature of the excitations, the relevant microscopic light scattering mechanisms and the electronic energy band structure of the solids. Results of work on the following problems are summarized:

(1) Resonance Raman Scattering as a Probe of Space Charge Fields at → next page

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20. ABSTRACT CONTINUED

cont. Semiconductor Surfaces;
(2) Raman Scattering and Light Diffraction by Surface Poloritons;
(3) Surface-Electromagnetic Wave Enhancement of Raman Scattering and Nonlinear Optical Phenomena;
(4) Giant Raman Scattering by Molecules Adsorbed on Metal Surfaces; and
(5) Inelastic Light Scattering by Charge Carriers in Two-Dimensional Plasmas

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RAMAN SPECTROSCOPY OF SOLIDS

U. S. ARMY RESEARCH OFFICE (DURHAM)

FINAL REPORT

Principal Investigator: Elias Burstein, Professor of Physics

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I STATEMENT OF THE KEY PROBLEMS STUDIED

Research on the inelastic scattering of light by elementary excitations in solids has provided information about the nature of the excitations, the relevant microscopic light scattering mechanisms and the electronic energy band structure of the solids. Our own work in this area has focussed on the following problems:

1. Resonance Raman Scattering As a Probe of Space Charge Fields at Semiconductor Surfaces
2. Raman Scattering and Light Diffraction by Surface Poloritons
3. Surface-Electromagnetic Wave Enhancement of Raman Scattering and Nonlinear Optical Phenomena
4. Giant Raman Scattering by Molecules Adsorbed on Metal Surfaces
5. Inelastic Light Scattering by Charge Carriers in Two-Dimensional Plasmas.

II SUMMARY OF IMPORTANT RESULTS

1. Resonance Raman Scattering As a Probe of Space Charge Fields at Semiconductor Surfaces [1,5,8,9].

Our studies of resonance enhanced Raman scattering by LO phonons at (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces InAs, which terminate in group III atoms (In) and in group V atoms (As) respectively, show that the energy bands at the (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces of both n- InAs and p- InAs are bent upwards in the direction of the outward normal. We find further that in the case of moderately doped samples of both n- and p- InAs (e.g. $10^{17}/cm^3$) the surface space charge field (e.g. band bending) at the (111) surface is smaller than that at the ($\bar{1}\bar{1}\bar{1}$) surface. In samples of p- InAs with increasing charge densities the surface electric field on the (111) surface becomes vanishingly small, while that at the ($\bar{1}\bar{1}\bar{1}$) surface increases in magnitude. On the other hand, in samples of n- InAs with high comir densities, the surface electric fields at (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces are both large. The difference in the surface space charge fields at the (111) and ($\bar{1}\bar{1}\bar{1}$) surfaces of n- and p- InAs reflect the differences in the surface states and consequent differences in the pinning of the Fermi level at the surface.

We have also investigated the resonance Raman scattering by LO phonons and coupled LO-phonon-plasmon modes at n- and p- InAs surfaces in MOS devices (Ni - SiO2 - InAs). Our data show that it is readily possible to establish from the presence or absence of scattering by coupled LO phonon-

plasmon modes whether, for a given gate voltage, the surface of the n- or p- type InAs substrate was accumulated, depleted or inverted. Our data also showed that unlike the (111) surface of n- InAs in air which is depleted, the (111) surface of n- InAs in the unbiassed MOS device is accumulated, and furthermore that the (100) and (111) surface of p- InAs in the MOS devices are inverted, whereas (110) surface of p- InAs is accumulated.

2. Raman Scattering and Light Diffraction by Surface Polaritons [2,4,6,7].

Our theoretical analysis of the relative forward and backward scattering efficiencies of volume optical phonons and surface polaritons (surface-electromagnetic waves) indicates that the scattering efficiency of the surface polaritons at a single-interface configuration is a factor of 10^{-3} to 10^{-4} smaller than that of volume optical phonons in a backward scattering configuration, but is comparable to that of the volume optical phonons in a forward scattering configuration. It accounts for the fact that Raman scattering by surface polaritons at III - V compound semiconductor surfaces can only be readily observed under strong resonance-enhanced forward scattering conditions, i. e., at frequencies near the E_1 gap, where the medium is opaque, using thin films whose thickness is comparable to the skin depth. Our theoretical formulation is also applicable to configuration in which the semiconductor (e.g. the nonlinear medium) is the surface inactive medium and the dielectric is the surface active medium, as well as to configurations in which the semiconductor is the surface active medium, indicate.

On the experimental side we have observed the diffraction of light by surface EM waves (i.e., surface polaritons) generalized by cw CO_2 laser radiation at a BeO - air interface in an Otto ATR prism configuration. The phenomenon is a three wave-mixing process in which an incident volume EM wave in the visible is parametrically mixed with a linearly-driven surface EM wave in the infrared to generate a second volume EM wave in the visible. It is one of a group of related three wave-mixing processes which includes the Raman scattering by surface polaritons in which an incident volume EM wave in the visible is inelastically scattered by thermally generated surface polaritons, the parametric mixing of two volume EM waves in the visible to generate a surface EM wave in the infrared.

By measuring the scattered intensity as a function of the position at which the incident visible EM radiation and the surface EM waves interact, we were able to determine the electric field profile at the BeO - air

interface. Also from the data on the spatial distribution of the diffracted light from the "free propagation" region, we derived a value of 44 micorns for the propagation length of the surface EM waves at 10.6 microns. Correcting for the radiative loss in the prism we obtain a value of ∿100 microns for the propagation length of the surface EM waves at BeO - air interface, in the absence of the prism, which is in reasonable agreement with the value ∿90 microns estimated form the complex dielectric constant of BeO.

3. Surface-Electromagnetic Wave Enhancement of Raman Scattering Nonlinear Optical Phenomena [10,11].

We have shown that, by using surface EM waves in an ATR prism configuration as the excitation radiation, it should be possible to enhance the intensity of Raman scattering by molecules near a Ag surface by one to two orders of magnitude over that in an external reflection (ER) configuration. Specifically the calculated enhancement of the (zz) scattering cross-section of a thin molecular overlayer on Ag at 6000Å resulting from the use of surface EM waves for a Kretschmann (prism - Ag film - air) configuration (for a prism with a refractive under of 1.5 and an optimum Ag film thickness of 530Å) is ∿340. The corresponding enhancement which results from a mixed prism-ER configuration in which the incident radiation is a surface - EM wave and the scattered radiation is a volume - EM wan (in air) is ∿100. Our data on the Raman scattering by liquid benzene, as the surface-inactive dielectric medium adjoining the Ag film, in a mixed prism - ER configuration yield (on the basis of the penetration depth (∿2000Å) of the surface - EM waves in the liquid benzene) an enhancement of ∿75 in good agreement with the theoretically estimated value of 70.

We have also carried out a general formulation of nonlinear optical phenomenon (e.g., second harmonic generation, parametric three-wave mixing etc.) which encompasses the ATR prism configuration and the ER configuration. The formulation takes into account the "transfer" of EM radiation into and out of the nonlinear medium, which are different for the two configuarations and the kinematical factors of the nonlinear interaction which, for the most part, are essentially the same for surface - EM and volume EM waves. Because of the dispersion of the surface - EM waves at the Ag - air interface it is not possible to have colinear surface - EM waves as the incoming and output waves in second harmonic generation. As a consequence, the enhancement in the input transfer factor when surface - EM waves are used as the input waves in the prism configuration is offset by the dimunition of the output transfer

factor when the output waves are evanescent EM waves, and one can obtain an enhancement of the input transfer factor.

4. Giant Raman Scattering by Molecules Adsorbed on Metal Surfaces, 13, 14, 15, 17.

We have proposed that the microscopic mechanisms for the very large ("giant") enhancement of the RS by adsorbed pyridine and CN^- on electrochemically processed Ag electrodes involves surface roughness enhanced electron-hole pair excitations on the surface region of the metal and/or charge transfer excitations of the metal-adsorbed molecule complex. We have furthermore suggested that the sub-microscopic surface roughness that is produced by the electrochemical processing of the Ag electrode makes possible the adsorption of molecules by the metal which might otherwise not occur on a smooth surface and also leads to the appearance of transverse collective-excitations of the charge carriers, whose excitation by either s- or p-polarized EM radiation leads to enhanced EM fields at the adsorbed molecules.

On the experimental side we have studied the strong Raman scattering continuum that accompanies the enhanced RS by adsorbed molecules on Ag. The Raman scattering continuum which extends beyond 4000 cm^{-1} is similar in character to the RS by electrochemically roughened Ag electrodes in the absence of adsorbed molecules. We have therefore suggested that it is due to surface roughness enhanced inelastic light scattering by particle-hole excitations in the metal.

We have also shown that molecules such as isonicotinic acid and benzoic acid adsorbed on thin ($\sim$50Å mass thickness) Ag island (e.g., aggregated) films exhibit a strongly Raman scattering which is comparable in intensity and similar in character to that observed for pyridine and CN^- adsorbed on electochemically processed Ag electrodes, and which is also accompanied by a strong inelastic light scattering continium. As in the case of electrochemically processed Ag electrodes the Raman scattering by the adsorbed molecules on the Ag island films, and the inelastic light scattering continuum which is also exhibited by Ag island films in the absence of adsorbed molecules, an insensitive to the polarization and angles of the incident and scattered radiation.

5. Inelastic Light Scattering by Charge Carriers in Two Dimensional Plasmas 12, 16.

We have carried out a theoretical analysis of the inelastic scattering of

light by inter-subband carrier excitations in two dimensional plasmas that occur at semiconductor surfaces, and have shown that it should be readily feasible to observe such scattering under resonance-enhanced conditions and to obtain, thereby, information about both the single particle and collective inter-subband excitations.

We have also investigated the nature of the coupled modes that occur in polar semiconductors as a result of the coupling of LO phonons with the collective inter-subband excitations of the two-dimensional plasmas. These modes are the analogs of the coupled LO phonon-plasmas modes in bulk semiconductors.

The inelastic light scattering by non-spin-flip and spin-flip inter-subband excitations has, in fact, now been reported by Abstreiter and Ploog (Phys Rev. Letters 42, 1308 (1979)) and by Pinczuk, Stormer, Dingle, Warloch, Wiegmann and Gossard (Solid State Communications 32, 1001 (1979)). The Scattering processes which contribute to inelastic scattering by the inter-subband excitations in non-polar semiconductors include the two-step and the three-step "carrier density" scattering mechanisms which are only applicable to scattering at the Eo and Eo + Δo optical gaps. In polar semiconductors we may expect sizeable contributions to the inelastic scattering by coupled LO phonon collective inter-subband excitations to come from Frohlich, electro-optic and deformation potential scattering processes at the E_1 and $E_1 + D_1$ gaps.

III LIST OF PARTICIPATING PERSONNEL

Stephen Buchner	Graduate student 1972 to 1976; Ph. D. January 1976 "Resonance-Enhanced Allowed, Field Induced and Wave Vector Dependent Scattering From the Surface Region of InAs"
Yung Jui (Ray) Chen	Graduate student 1972 to 1976; Ph. D. January 1976 "The Role of Surface Electromagnitic Waves in Nailinear Optical Phenomena; "Research Investigator 1976
Chung Yueh Chen	Graduate student supported by NSF receiving partial support from ARD 1976 to 1979. Ph. D. expected June 1980. "Giant Raman Scattering by Adsorbed Molecules on Metal Surfaces
Li Yi Ching	Graduate student 1974 to 1979; Ph. D. expected June 1980 "Resonance Raman Scattering as Probe of Space Charge Region of Semiconductor Surface in MOS Structures"

Dr. Ivan Davoli	Research Investigator 1978 to 1979 working on Optical Phenomena at Metal Surfaces in Ultrahigh Vaccuum.
Steve Wollins	Graduate student 1977 to 1979 M.A. September 1979

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